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(57) Abstract

A method for preparing a plugging liquid for plugging of a zone of a subterranean formation around a bore hole, consisting of an emulsion comprising a continuous phase based on a hydrophobic liquid and a discontinuous phase based on a hydrophilic liquid, which emulsion contains an emulsifier, a polysaccharide and a cross–linking agent for said polysaccharide. The emulsifier and the cross–linking agent for the polysaccharide are introduced into and mixed with the hydrophobic liquid in any desired sequence, whereupon the hydrophilic liquid is introduced gradually into the prepared mixture under agitation, and the polysaccharide is then introduced, whereby a stable emulsion is obtained.

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A method for producing a plugging liquid on a polysaccharide basis.

This invention relates to a method for preparing a plugging liquid on emulsion basis and on polysaccharide basis for plugging a zone of a subterranean formation penetrated by a bore hole.

A large number of gel forming or thickening compositions are known for use as well control liquids in the drilling of wells for recovery of oil and gas, for instance in cases where a well liquid is lost to the formation, or liquid or gas is flowing into the well from the formation. It is previously known to use polysaccharides for thickening purposes in such known plugging liquids.

Thus, for plugging a zone of a subterranean formation around a bore hole, Norwegian Patent Application No. 931954 discloses a plugging liquid consisting of an emulsion comprising:

a) 5 - 50% by volume of a continuous phase containing:
   - 800 - 998.5 ml/l of a hydrophobic liquid,
   - 0.5 - 100 ml/l of an emulsifier, and
   - 1 - 100 g/l of a crosslinking agent for a polysaccharide,

b) 50 - 95% by volume of a discontinuous phase containing:
   - 950 - 997 ml/l of water, and
   - 3 - 50 g/l of a polysaccharide.

When this plugging liquid is subjected to high shear forces, e.g. by being forced through the nozzles of a drill bit, wherein the pressure drop will be in the range of about 50 to 120 bars, it thickens to a gelatinous solid. The mechanism of the thickening of the plugging liquid is a crosslinking of the polysaccharide with the crosslinking agent. It is therefore decisive for the performance of the plugging liquid that the polysaccharide and the crosslinking agent be kept separated from one another until the thickening of the drilling liquid is desired. According to said NO 931954, such separation is obtained by said crosslinking agent being contained in the

hydrophobic liquid (e.g. an oil), whereas the polysaccharide is contained in the discontinuous phase of the emulsion, which is an aqueous phase.

As long as the emulsion is at rest or is only subjected to moderate shear forces, the polysaccharide and the crosslinking agent remain separated from one another in their respective phases of the emulsion and no crosslinking reaction of any significance takes place. In this condition (Condition 1), the plugging liquid will have physical characteristics allowing it to be easily pumped, e.g. through a mud system. However, when the emulsion is subjected to high shear forces, e.g. by being forced through a drill bit in a bore hole, the polysaccharide and the crosslinking agent will come into contact with one another, whereby crosslinking of the polysaccharide takes place and the plugging liquid thickens.

For the plugging liquid to fulfil its function it is important that it (1) has the lowest possible viscosity in Condition 1, before it is subjected to high shear forces, (2) thickens to a high thickness in Condition 2 after having been subjected to high shear forces, (3) maintains its acquired thickness for a desired period of time, and (4) to the least possible extent undergoes a thickening in Condition 1 as a result of the emulsion gradually deteriorating during storage or before having passed through the nozzles of the drill bit in the bore hole. The plugging liquid according to NO 931954 satisfies these requirements to a surprisingly high extent.

However, the plugging liquid disclosed in NO 931954 is encumbered with certain disadvantages regarding its preparation *per se*, because the preparation necessitates using two mixing tanks, viz. one tank for mixing those components which should constitute the continuous hydrophobic phase (the oil phase), and one tank for mixing those components which should constitute the discontinuous phase (the aqueous phase). This has been considered to be necessary in order to maintain the polysaccharide separated from the crosslinking agent until the

time of the desired reaction between them, usually after said emulsion having been forced through the nozzles of the drill bit in the bore hole. Such production process requiring two mixing tanks will require more space than would be desirable, e.g. on an offshore oilrig.

It has now been found that the same effect of keeping the polysaccharide and the crosslinking agent separated from one another until a reaction between them is desired can be achieved by using a different method requiring less space and equipment.

Thus, the invention now provides a method for preparing a plugging liquid for plugging of a zone of a subterranean formation around a bore hole, consisting of an emulsion comprising a continuous phase based on a hydrophobic liquid and a discontinuous phase based on a hydrophilic liquid, which emulsion contains an emulsifier, a polysaccharide and a crosslinking agent for said polysaccharide. The method is characterized thereby that the emulsifier and the crosslinking agent for the polysaccharide - in any desired sequence - are introduced into and mixed with the hydrophobic liquid, whereupon the hydrophilic liquid is introduced gradually into the prepared mixture under agitation, and the polysaccharide is then introduced, whereby a stable emulsion is obtained.

In the new method only one mixing tank is used, instead of the two mixing tanks utilized in the previously disclosed method. This makes the new method less space and equipment requiring and less exposed to pollution from conduit systems, pumps, etc., than the method disclosed in NO 931954.

The hydrophilic liquid of the emulsion, which is usually water, will acquire a small content of polysaccharide. This results in the emulsion developing some viscosity which contributes to the forming of a stable emulsion.

As already mentioned, the prepared plugging liquid is stable and is normally not affected by being pumped with a centri-

fugal pump or a mud pump for several hours. However, extended agitation/pumping should be avoided beyond the point where a stable emulsion has been formed, to avoid an unintended thickening of the emulsion in Condition 1 as a result of the crosslinking agent coming in direct contact with the polysaccharide, whereby crosslinking takes place. This is especially important when e.g. a cement is used as a crosslinking agent.

On the other hand, when the emulsion is subjected to high shear forces, such as when forced through the nozzles of a drill bit at a pressure drop of 40 to 120 bars, e.g. about 60 bars, the emulsion thickens markedly after 2 to 10 minutes. If desired, however, the thickening time can be made shorter.

The hydrophobic liquid of the plugging liquid of the invention may advantageously be selected from mineral oils, vegetable oils, esters and ethers. It is selected on the basis of conventional criteriae such as viscosity, stability, compatibility with the drilling mud, environmental leniency and availability.

For the purpose of obtaining a stable emulsion a suitable emulsifier is included in the continuous phase. The emulsifier can be selected from a broad range of commercially available emulsifiers. The emulsifier should preferably have an alkali resistance such that it is stable in the pH range of 11 to 13 at typical bore hole temperatures. Emulsifiers on a triglyceride basis are very suitable for use in the plugging liquid. Based on conventional criteriae which will be well known to those skilled in the art, such combinations of hydrophobic liquid and emulsifier are selected which will provide the desired pH stability and the desired emulsion strength for handling and storing the emulsion, but which result in a breaking of the emulsion when the emulsion is pumped for instance through the nozzles of a drill bit down in a bore hole or through a port in a completion string.

The polysaccharide serving to achieve the desired hardness of the emulsion in Condition 2 may for instance be selected from

any of the polysaccharides previously utilized for well control. The currently most preferred polysaccharides are xanthanes, alginates and carboxymethyl cellulose, due to their combination of good crosslinking properties and viscosity characteristics.

Any of the commonly used crosslinking agents for polysaccharides may be used, especially such crosslinking agents that are stable at pH values in the range of 11 to 13. A preferred class of crosslinking agents is constituted by those containing divalent or trivalent metal ions as the active moiety. Examples of such crosslinking agents are $Ca(OH)_2$, $CaSO_4$ and $Al_2(SO_4)_3$. Another example is a cement, e.g. of Class G, which in addition to performing satisfactorily as a crosslinking agent will also confer a high thermal stability to the emulsion. Another class of preferred crosslinking agents is constituted by aldehydes, such as glutaric aldehyde.

In addition to the above-mentioned main constituents the plugging liquid may contain a water-absorbing material in the continuous phase, i.e. the "oil" phase. Thus, the water-absorbing material is introduced into the mixture before the hydrophilic phase, usually water, is added. As water-absorbing material, a clay mineral would be preferred, in particular bentonite. By being incorporated in the "oil" phase, the water-absorbing material will be kept separated from the water contained in the aqueous phase, until the emulsion is broken by being subjected to high shear forces. The water-absorbing material will then come into contact with the water contained in the aqueous phase of the emulsion and will absorb excess amounts thereof, whereby said material will undergo swelling, as explained in US Patent No. 4,663,366. However, in the plugging liquid prepared by the method of the invention, the function of the water-absorbing material is not primarily to provide the thickening of the liquid aimed at in said US patent but to absorb free water after the breaking of the emulsion and thus to prevent a shrinking of the material in Condition 2.

In Condition 1 the plugging liquid should be maintained under gentle agitation and at a liquid temperature below 40°C. In preferred embodiments the plugging liquid contains no environmentally harmful or noxious constituents.

As mentioned above, the plugging liquid is usually not affected by being pumped with a centrifugal pump or mud a pump for several hours. However, when the emulsion is subjected to high shear forces, it thickens markedly after 2 to 10 minutes. The thickening time can be predetermined through an appropriate selection of the amounts of crosslinking agent and emulsifier, especially of the amount of emulsifier. An increased amount of emulsifier increases the thickening time, whereas an increased amount of crosslinking agent reduces the thickening time.

In the method of the invention, the constituents are preferably mixed in such amounts as to form an emulsion which per 100 parts by volume of hydrophobic and hydrophilic liquid contains 5 to 50 parts by volume of hydrophobic liquid and 95 to 50 parts by volume of hydrophilic liquid, which emulsion further contains 0.5 to 100 ml/l of emulsifier, 3 to 50 g/l of polysaccharide, and 1 to 200 g/l of crosslinking agent for the polysaccharide, based on the total amount of emulsion.

More preferably, the constituents are mixed in such amounts as to form an emulsion which per 100 parts by volume of hydrophobic and hydrophilic liquid contains 10 to 30 parts by volume of hydrophobic liquid and 90 to 70 parts by volume of hydrophilic liquid, which emulsion further contains 1 to 50 ml/l of emulsifier, 3 to 30 g/l of polysaccharide, and 2 to 50 g/l of crosslinking agent for the polysaccharide, based on the total amount of emulsion.

The plugging liquid prepared by the new method may be given a content of a weighting material in addition to the constituents already mentioned, whereby the plugging liquid may be used for inhibiting or preventing undesired blow-outs into or from a well bore. The purpose of using a weighting material in the plugging liquid is to increase the density thereof so as

to put the plugging liquid in a better condition to resist the blow-out pressure in the well bore. In the method of the invention, the weighting material is added after the hydrophilic phase, e.g. water, and the polysaccharide, have been added.

Any weighting material can be used in the weighted plugging liquid. Exemplary weighting materials are barite, ilmenite, hematite, steel balls and calcium carbonate. A particularly suitable weighting material is barite.

The other constituents of the weighted plugging liquid, i.e. the hydrophobic liquid, the emulsifier, the polysaccharide, the crosslinking agent for the polysaccharide, and the hydrophilic liquid, are selected as for the non-weighted plugging liquid, as has been described above in connection with the preparation of the non-weighted plugging liquid.

When the plugging liquid is to be used for permanent closing of a bore hole, the plugging liquid may if desired contain an additive to prevent circulation loss, such as crushed nut shells or mica folium. This additive is added at the end, optionally together with the weighting material, if such material is also used.

The mud system employed in well and formation treatment operations consists of a number of units, each of which exerts shear stress to a greater or lesser extent on the flowing liquid. The shear stress is closely related to the pressure drop in each individual unit. The highest pressure drop and thus the highest shear stress occurs e.g. during the passage of a port in a completion string or the nozzles in a drill bit. The use of the prepared plugging liquid is based on the condition that only flow restrictions down in the well should produce a sufficiently high shear stress for the reactants (polysaccharide and crosslinking agent) to come into contact with one another, with a resulting crosslinking of the polysaccharide and a setting of the liquid.

The invention is shown in more detail in the following examples.

Example 1

About 1 liter of an emulsion of the water-in-oil type was prepared by adding to 100 ml of linear α-olefin under agitation 2.2 ml of fatty acid emulsifier and 6 grams of $Ca(OH)_2$, whereupon 900 ml of water were added gradually under continued agitation. 6 grams of xanthane gum were then added under agitation to the obtained emulsion. Finally, the emulsion was stabilized by being stirred for 5 minutes.

The obtained stabilized emulsion was pumped at a pressure of 50 bars through a nozzle and down into a cup, wherein it set in the course of 2 minutes. After 24 hours the shear stress was measured to be 6000 Pa.

Example 2

About 1 liter of an emulsion of the water-in-oil type was prepared by adding to 250 ml of linear α-olefin under agitation 2.5 ml of fatty acid emulsifier, 25 grams of bentonite, and 6 grams of $Ca(OH)_2$, whereupon 750 ml of water were added gradually under continued agitation. 10 grams of alginate were then added under agitation to the obtained emulsion. Finally, the emulsion was stabilized by being stirred for 5 minutes.

The obtained stabilized emulsion was pumped at a pressure of 50 bars through a nozzle and down into a cup, wherein it set in the course of 0.5 minute. After 24 hours the shear stress was measured to be 9000 Pa.

Patent claims

1. Method for preparing a plugging liquid for plugging of a zone of a subterranean formation around a bore hole, consisting of an emulsion comprising a continuous phase based on a hydrophobic liquid and a discontinuous phase based on a hydrophilic liquid, which emulsion contains an emulsifier, a polysaccharide and a crosslinking agent for said polysaccharide, **characterized** thereby that the emulsifier and the crosslinking agent for the polysaccharide - in any desired sequence - are introduced into and mixed with the hydrophobic liquid, whereupon the hydrophilic liquid is introduced gradually into the prepared mixture under agitation, and the polysaccharide is then introduced, whereby a stable emulsion is obtained.

2. Method according to claim 1, **characterized** in that water is used as the hydrophilic liquid.

3. Method according to claim 1 or 2, **characterized** thereby that as hydrophobic liquid there is used a liquid selected from mineral oils, vegetable oils, esters, ethers and α-olefin oligomers.

4. Method according to any of claims 1 to 3, **characterized** in that the constituents are mixed in such amounts as to form an emulsion which per 100 parts by volume of hydrophobic and hydrophilic liquid contains 5 to 50 parts by volume of hydrophobic liquid and 95 to 50 parts by volume of hydrophilic liquid, which emulsion further contains 0.5 to 100 ml/l of emulsifier, 3 to 50 g/l of polysaccharide, and 1 to 200 g/l of crosslinking agent for the polysaccharide, based on the total amount of emulsion.

5. Method according to claim 4, **characterized** in that the constituents are mixed in such amounts as to form an emulsion which per 100 parts by volume of hydrophobic and hydrophilic liquid contains 10 to 30 parts by volume of hydrophobic liquid and 90 to 70 parts by volume of hydrophilic liquid,

which emulsion further contains 1 to 50 ml/l of emulsifier, 3 to 30 g/l of polysaccharide, and 2 to 50 g/l of crosslinking agent for the polysaccharide, based on the total amount of emulsion.

6. Method according to any of claims 1 to 5, **characterized** by there being used an emulsifier having an alkali resistance such that the plugging liquid is stable at pH 11 to 13.

7. Method according to claim 6, **characterized** by there being used an emulsifier on a triglyceride basis.

8. Method according to any of claims 1 to 7, **characterized** by there being used as polysaccharide a xanthane, an alginate or a carboxymethyl cellulose.

9. Method according to any of claims 1 to 8, **characterized** by there being used a crosslinking agent containing divalent or trivalent metal ions as the active moiety.

10. Method according to claim 9, **characterized** in that a cement is used as crosslinking agent.

11. Method according to any of claims 1 to 8, **characterized** in that an aldehyde is used as crosslinking agent.

12. Method according to any of claims 2 to 11, **characterized** in that a water absorbing material is also incorporated into the mixture on hydrophobic liquid basis, before the water is incorporated into said mixture.

13. Method according to claim 12, **characterized** by there being used as water absorbing material a clay material, especially bentonite.

14. Method according to any of claims 2 to 13, for preparing a weighted plugging liquid, **characterized** in that a weighting material is added after the water has been added.

15. Method according to claim 14, **characterized** by there being used a weighting material selected from barite, ilmenite, hematite, steel balls and calsium carbonate.

16. Method according to claim 15, **characterized** in that barite is used as weighting material.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 98/00179

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C09K 7/06, E21B 33/13
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C09K, E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EPODOQ, USPATFULL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9428085 A1 (DEN NORSKE STATS OLJESELSKAP A.S.), 8 December 1994 (08.12.94), page 4, line 10 - page 5, line 32; page 9, line 12 - page 11, line 8, Claims --	1-16
A	Derwent's abstract, No 89-307380/42, week 8942, ABSTRACT OF SU, 1447-832 (Ukhtinsk Industrial), 30 December 1988 (30.12.88) --	1-16
A	EP 0137538 A2 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.), 17 April 1985 (17.04.85) -- --------	1-16

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Information on patent family members

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